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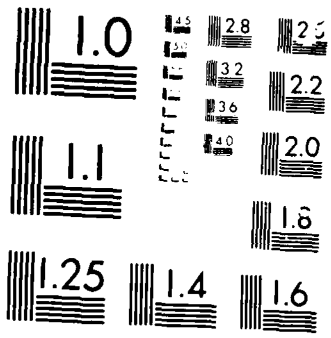
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Mechanics and Materials Center
TEXAS A&M UNIVERSITY
College Station, Texas

STRESS EFFECTS ON MOISTURE TRANSPORT IN AN EPOXY RESIN AND ITS COMPOSITE

Y. WEITSMAN AND M. HENSON

OFFICE OF NAVAL RESEARCH
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This paper presents the results of an experimental investigation of stress effects on the sorption of water vapor in an epoxy resin and its composite. Such effects were noted by several researchers in both polymers [1]-[3] and composites [4], although these earlier investigations did not present a comprehensive study of the phenomenon. This paper summarizes results which were obtained recently [5], and the interested readers are referred to [5] for complete details.

It is shown that in both epoxy and graphite/epoxy composites, external stresses affect the diffusion process. In the case of the resin, stresses appear to raise the moisture saturation levels while in composites stresses appear to affect the entire sorption process, accentuating the a-symmetries between absorption and desorption behavior. In both materials the moisture transport process departs both quantitatively and qualitatively from the predictions of classical, Fickean diffusion.

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STRESS EFFECTS ON MOISTURE TRANSPORT
IN AN EPOXY RESIN AND ITS COMPOSITE

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ABSTRACT

This paper presents the results of an experimental investigation of stress effects on the sorption of water vapor in an epoxy resin and its composite. Such effects were noted by several researchers in both polymers [1]-[3]# and composites [4], although these earlier investigations did not present a comprehensive study of the phenomenon. This paper summarizes results which were obtained recently [5], and the interested readers are referred to [5] for complete details.

It is shown that in both epoxy and graphite/epoxy composites, external stresses affect the diffusion process. In the case of the resin, stresses appear to raise the moisture saturation levels, while in composites stresses appear to affect the entire sorption process, accentuating the a-symmetries between absorption and desorption behavior. In both materials the moisture transport process departs both quantitatively and qualitatively from the predictions of classical, Fickean diffusion.

EXPERIMENTAL

The experimental program involved the measurement of moisture weight-gain in resin and composite coupons that were subjected to several stress levels.

(a) Materials and Specimen Preparation.

The resin and composite materials were Hercules 3502 epoxy and AS4/3502 graphite/epoxy, respectively.

The resin was cast between two pyrex glass plates, then cured under vacuum and post cured in an air circulating oven at 204°C (400°F) for four hours. Unidirectional, six ply, graphite/epoxy panels were fabricated in an air cavity press according to manufacturer's specifications, then post cured at 400°F for four hours.

Tensile coupons, of dimensions 12.7 x 12.7 x 0.76 cm (5" x 0.5" x 0.03") were cut from both epoxy and composite panels. In the latter case, all fibers were oriented transversely to the load direction. All coupons were tabbed with 304 stainless steel tabs, which were bonded with the 3M AF-163-2K structural

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#Numbers in brackets indicate reference cited at the end of this paper.

adhesive. Bonding was achieved by curing the adhesive in an air circulating oven. The tabbed coupons were then dried in a vacuum oven at 93°C (200°F) for about two days, until they attained equilibrium weights.

Complete details of the various curing processes and the coupons dimensions are given in Ref. [5].

(b) Moisture Weight-Gain Measurements.

The essential part of this investigation involved the determination of the amounts of moisture absorbed and desorbed by resin and composite coupons under various stress levels.

The stress-dependent moisture content was determined by loading the specimens inside environmentally controlled chambers and removing them periodically for weight measurements.

Absorption tests were performed by placing a container of distilled water heated to 40°C (104°F) at the bottom of an environmental chamber, producing a relative humidity of 97%. Desorption of saturated samples was achieved by placing dessicant bags inside the chambers, resulting in a relative humidity of 0%. Circulating fans were used to provide uniform environmental conditions throughout the chambers, whose temperature of 40°C was monitored by thermocouples.

A stainless steel load frame was placed within each chamber, supporting up to six specimens under constant loads as shown in Fig. 1. Specimens in

Figure 1: The load frame and environmental chamber employed for acquiring the moisture sorption data.

two series, each containing three coupons, were loaded through momentless pin connections so as to produce pure uniaxial tension. Loads were applied by hanging lead weights below the specimens. All stress levels were related to the dry ultimate tensile stress of the 3502 epoxy, namely $\sigma_{ult} = 51.7$ MPa (= 7500 psi). Thus, both epoxy and composite coupons were subjected to the same stress levels. The moisture weight-gain measurements were performed on a Mettler HL 32 electronic balance with resolution of 10^{-4} grams.

The test program for moisture sorption is shown in Table 1. Note the number of replicate tests, whose purpose was to assess data scatter.

(c) Deformation Measurements.

These measurements involved the determination of moisture-induced swelling strains, and the recording of creep and recovery strains under constants stresses.

The creep and recovery data were collected at room temperature. These involved dry resin specimens and wet composite coupons, as well as samples that were previously saturated at 97% RH at 40°C under several stress levels. Creep strains were recorded at stress levels of up to 45% of σ_{ult} to assess the range of linearity of the stress-strain response.

Number of Weight Gain Specimens	Number of Axial Deformation Specimens	Stress Level percent of neat resin UTS*
6	3	0%
6	2	15%
6	2	30%
4	2	45%

Table 1. Absorption and desorption test plan for 3502 epoxy resin and AS4/3502 graphite epoxy (*Neat resin UTS = 51.68 MPa (7500 psi))

The moisture induced swelling was monitored in sets of three replicate samples each of epoxy and composite coupons. The deformation was measured by a set of dial calipers, accurate to 0.0025 cm (10^{-3} inch).

(d) Material Properties Measurements.

These measurements involved the determination of the dry glass transition temperature and of basic mechanical properties. The results are given in Tables 2,3, and 4 below.

Material	Glass Transition Temperature (°C)	
	DSC II	Rheometrics Unit
Dry-Unconditioned 3502 Epoxy Resin	251	243
Dry-Unconditioned AS4/3502 Graphite Epoxy	240	243

Table 2. Glass Transition Temperatures for 3502 epoxy resin and AS4/3502 graphite epoxy.

Specimen	Ultimate Stress		Ultimate Strain	Modulus	
	(MPa)	(ksi)	(%)	(GPa)	(Msi)
10-Dry Unconditioned ASTM Dogbones	5.17	0.75	1.340	4.28	0.62
3-Dry Unconditioned Tensile Coupons	3.43	0.49	0.847	4.14	0.60
1-Desorbed Coupon Previously Unstressed During Diffusion	3.82	0.55	0.919	4.48	0.65
1-Desorbed Coupon Previously at 45% UTS During Diffusion	2.35	0.34	0.476	4.55	0.66

Table 3. Average tensile stress-strain results for 3502 epoxy resin at room temperature (RT). (Strain Rate = .005 in/in/min)

Specimen	Ultimate Stress		Ultimate Strain	Modulus	
	(MPa)	(ksi)	(%)	(GPa)	(Msi)
2-Dry Unconditioned Tensile Coupons	6.47	.94	.632	11.73	1.70
2-Wet Coupons Previously Unstressed During Absorption	4.07	.59	.392	11.31	1.64
2-Wet Coupons Previously at 45% UTS During Absorption	4.65	.67	.482	10.49	1.52

Table 4. Average tensile stress-strain results for transverse AS4/3502 graphite epoxy at RT. (Strain Rate = 0.005 in/in/min)

RESULTS

(a) Moisture Absorption and Desorption Under Stress.

The moisture content within the tensile coupons was calculated according to $M = (W - W_d)/\rho V$

where M denotes moisture content in % weight gain, W is the current wet weight of the coupon, W_d is the initial dry weight of the coupon, ρ is the dry density of the coupon's material and V is the volume of the dry material within the gage length of the tensile coupon.

Moisture absorption and desorption data are plotted vs. $\sqrt{t}$ in Figs. 2-5 for the epoxy resin and in Figs. 6-9 for the composite. Fig. 2 shows typical data scatter among replicate epoxy specimens. This scatter may be due to material variability as well as differences in the actual relative humidities and temperatures within the various chambers. It was noticed that the amplitude of the scatter increased with stress level, indicating susceptibility to mechanical flaws as well as possible variations in the true stress levels due to non-uniformities in the specimens' thicknesses. The average values of moisture up-take in epoxy vs. $\sqrt{t}$ at the four tested amplitudes of applied stress are shown in Fig. 3. Although there were overlaps between the scatter bands recorded for the individual stress levels, the trend towards increased moisture uptake with stress is consistent and unquestionable. Figs. 4 and 5 show the average values of moisture weight gain and weight loss in epoxy vs. $\sqrt{t}$ for unstressed coupons as well as for specimens stressed at 45% of σ_{ult}. In those figures the weight losses during desorption are referred to an initial time which starts at the beginning of the desorption process. Note the absence of hysteresis in Fig. 4 and the relatively small hysteresis loop even at $\sigma = 45\% \ \sigma_{ult}$ in Fig. 5. Nevertheless, it should be noted that due to technical difficulties with the periodic unloading and reloading of the specimens during the desorption stage, various mechanical failures occurred and fewer specimens survived to the termination of the desorption cycle. This fact renders the desorption data less reliable than the absorption information.

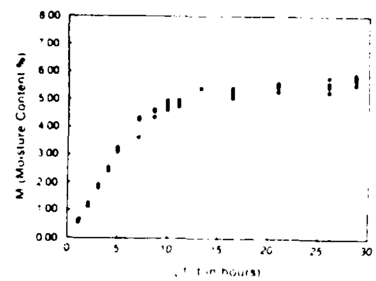


Figure 2. Moisture uptake vs. $\sqrt{t}$ in 3502 epoxy coupons subjected to $\sigma = 30\%$ UTS during absorption (97% RH, 40°C), with scatter among replicate specimens.

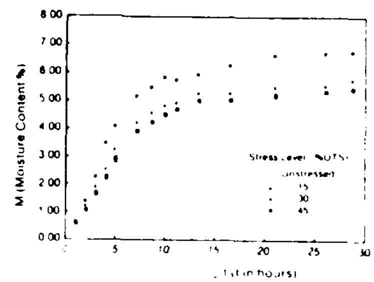


Figure 3. Average moisture uptake vs. $\sqrt{t}$ in 3502 epoxy coupons subjected to various stress levels during absorption (97% RH, 40°C).

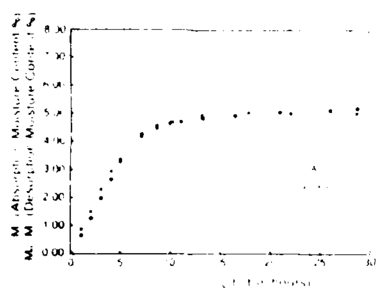


Figure 4. Superimposed average values of moisture content vs. $\sqrt{t}$ in unstressed 3502 epoxy coupons during absorption (97% RH) and desorption (0% RH), at 40°C.

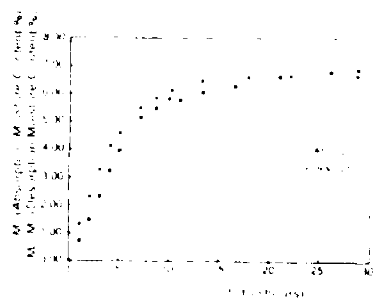


Figure 5. Same as Fig. 4 but under stress $\sigma = 45\%$ UTS.

Fig. 6 exhibits the data scatter encountered in composite samples. Note that this scatter, which grows with the level of applied stress, exceeds the spread in the resin's response. The average value of moisture-uptake in the composite vs. $\sqrt{t}$ is shown for the four tested stress levels in Fig. 7. It is interesting to note that under all stresses the moisture uptake follows the so-called "sigmoidally shaped" curve [6], in clear contravention of classical diffusion theory.

Fig. 8 exhibits a typical scatter band during desorption, which is characteristically wider than the scatter band during absorption.

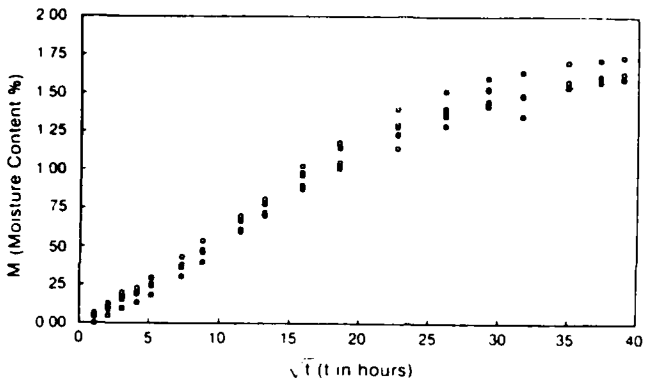


Figure 6. Moisture uptake vs. $\sqrt{t}$ in AS4/3502 composite coupons subjected to σ = 30% UTS during absorption (97% RH, 40°C), with scatter among replicate specimens.

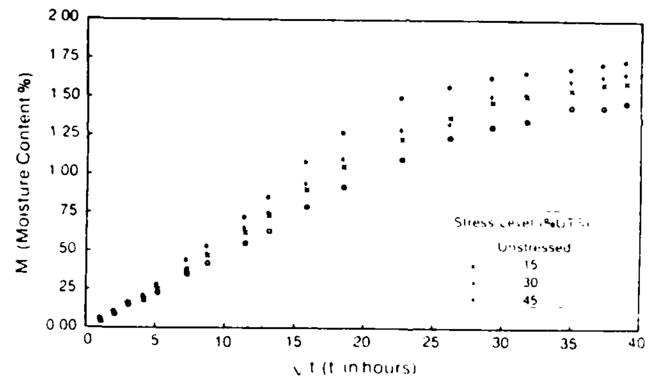


Figure 7. Average moisture uptake vs. $\sqrt{t}$ in AS4/3502 composite coupons subjected to various stress levels during absorption (97% RH, 40°C).

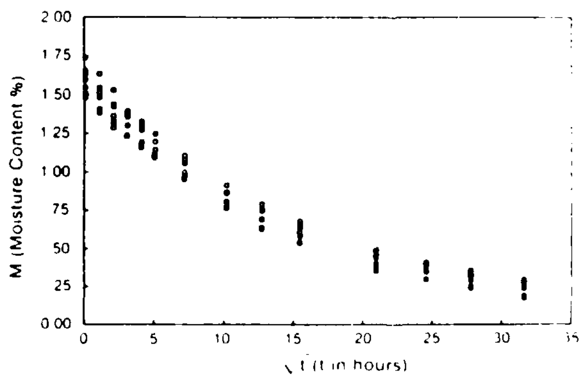


Figure 8. Moisture content vs. $\sqrt{t}$ in AS4/3502 composite coupons subjected to σ = 30% UTS during desorption (0% RH, 40°C), with scatter among replicate specimens.

Figs. 9(a),(b) and (c) show the average values of moisture weight-gain and weight-loss during absorption and desorption vs. $\sqrt{t}$ in the composite. As in Figs. 4 and 5 the average desorption data in Figs. 9(a)-(c) is presented relatively to a new initial time - the time since inception of desorption. Note the most significant hysteresis loops in Fig. 9, in marked contrast with Figs. 4 and 5. The amplitude of these loops is seen to increase with stress. Desorption data were also obtained under $\sigma = 45\%$ of σ_{ult} but most specimens failed before the termination of the desorption stage. It is therefore suspected that excessive creep and damage at 0.45 σ_{ult} would cause intractable scatter in the desorption measurements so as to render the information doubtful.

Note that all absorption tests were terminated after about 35 days for the epoxy specimens and after about 63 day for the composite coupons, at which times the weight gain increments tapered off considerably. Nevertheless, the data in Figs. 3 and 7 did not level off at those times, which implies that saturation had not yet been attained. The maximal moisture weight-gains are plotted vs. the stress level in Fig. 10. Note that M_{max} increases roughly linearly with stress for the composite coupons, but grows non-linearly for the epoxy samples.

The averaged data points in Figs. 3 and 7 were compared against predictions of classical diffusion, and the results are shown in Figs. 11 and 12. Note that in the case of epoxy (Fig. 11), the data for all stress levels fall consistently below the classical predictions. In Fig. 11, the classical results were forced to match the initial slopes of the various data sets, and coincide with M_{max} at $t = 840$ hours. On the other hand, the "sigmoidal" data sets in Fig. 12, which apply to the composite specimens, were compared against classical predictions which provided "best fits" with long-time measurements. In this circumstance the earlier data points tend to lie below the classical predictions.

Employment of the initial slopes of the data sets in Figs. 11 and 12 to determine values of equivalent "classical" diffusion coefficients, yields the values listed in Table 5 below.

Material	Stress Level (%) UTS)			
	0	15	30	45
Epoxy	2.29	2.41	2.44	3.21
Graphite/Epoxy	0.365	0.442	0.425	0.491

Table 5: Equivalent "classical" values of the coefficient of moisture diffusion D in 10^{-7} mm²/sec

Note that the values for the graphite/epoxy cannot be related to the resin's diffusivity by the standard "micro mechanics" formulae, i.e.

$$D_c = (1-v_f)D_r/(1+v_f), \quad \text{or} \quad D_c = D_r(1-2\sqrt{v_f/\pi})$$

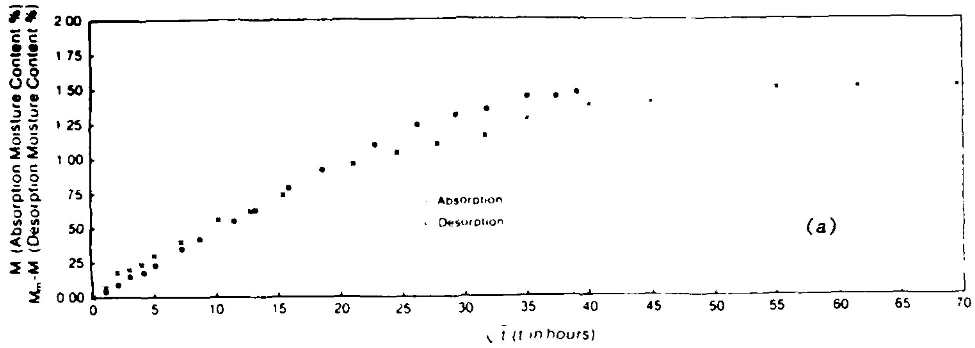
where the fiber volume fraction was $v_f = 0.66$ in the present case.

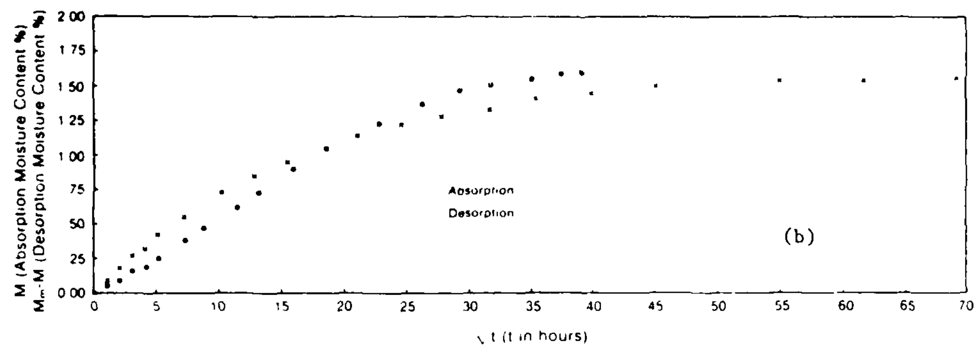
(b) Creep and recovery under stress.

Creep and recovery strains were recorded for dry epoxy coupons loaded under 30% and 40% of σ_{ult} for durations between 15 and 20 min. Upon release of the loads, recovery strains were measured for additional periods between 35 and 50 min. Some of the test coupons were subjected previously to stresses of 45% σ_{ult} while absorbing moisture.

Similar strains were recorded for uni-directional AS4/3502 gr/ep coupons, loaded transversely to the fiber direction, under stresses up to 45% σ_{ult}. Some coupons were tested dry, while others were tested wet - with previous history of exposure to moisture under various stresses.

Results for the resin and composite coupons are shown in Figs. 13(a) and 13(b), respectively. In those figures the compliance D(t) was determined by $D(t) = \varepsilon(t)/\sigma_o$, where σ_o denotes stress during the loading stage. The scatter in the creep data does not correlate with variations in stress levels, leading to the conclusion that, at least for sufficiently short times, the viscoelastic behavior of both resin and composite materials remains linear under stresses of up to 45% σ_{ult}. The negative strains recorded during recovery indicate that some slip could have occurred in the grips, or faulty bonds existed between coupons and tabs.





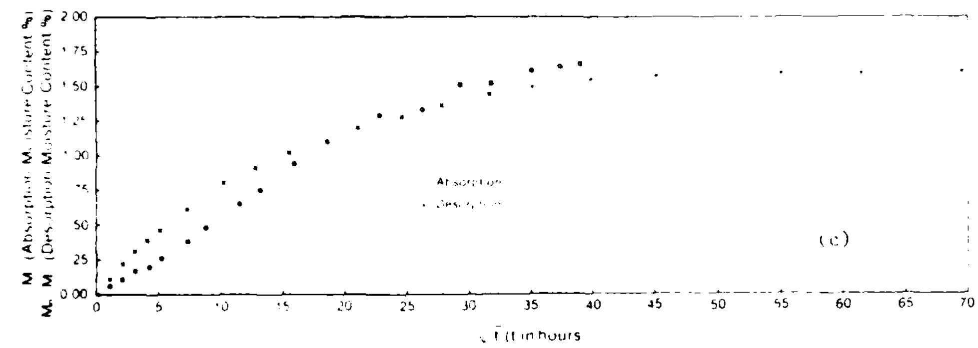


Figure 9(a),(b),(c). Superimposed values of average moisture content vs. $\sqrt{t}$ in AS4/3502 composite coupons during absorption (97% RH) and desorption (0%) at 40°C. (a) Unstressed (b) σ = 15% UTS (c) σ = 30% UTS.

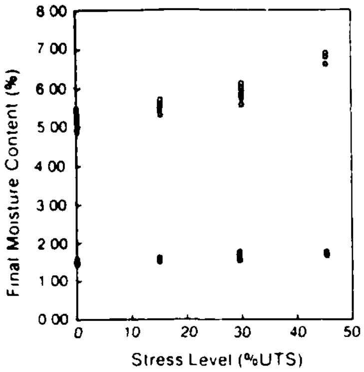


Figure 10. Maximal moisture content attained in absorption tests vs. stress level under exposure at 97% RH and 40°C. 3502 epoxy after 35 days (open circles) and AS4/3502 composite after 63 days (solid circles).

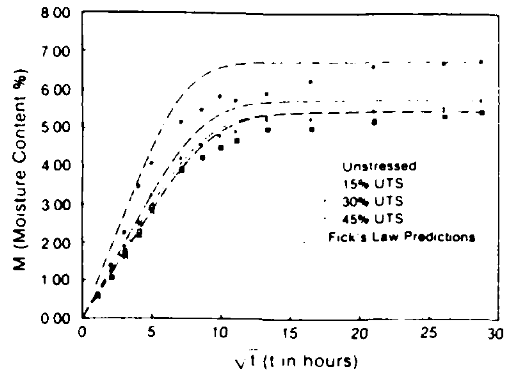


Figure 11. Comparison between average moisture uptake data for 3502 epoxy and predictions of classical diffusion theory.

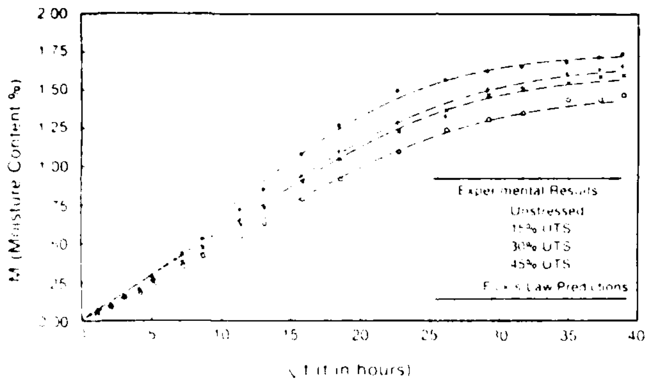


Figure 12. Same as Fig. 11 but for AS4/3502 composite.

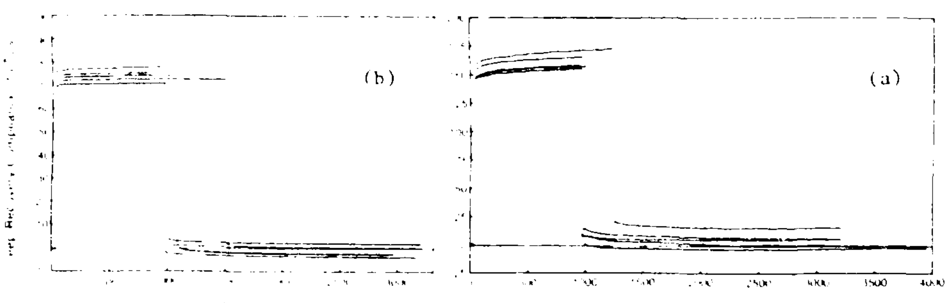


Figure 13. Creep and recovery compliance data for several coupons tested under stresses up to 45% σ_{ult}. (a) epoxy. (b) transversely loaded gr/ep composite.

CONCLUDING REMARKS

This paper presented a comprehensive investigation on stress assisted diffusion in 3502 epoxy and AS4/3502 graphite/epoxy coupons, under uni-axial tensile stresses.

The interaction between stress and moisture in epoxy, as well as the departures between the observed moisture uptake and predictions of classical diffusion, can be attributed to the time dependent response of the resin. These interactions were recently explained in the context of a constitutive model derived from basic concepts of continuum mechanics and irreversible thermodynamics [7].

In the case of composites, the interactions between stress and moisture diffusion are apparently due mainly to damage. This damage was observed to occur as profuse debondings at the fiber/matrix interfaces, with a strong propensity for coalescence into continuous cracks [8],[9]. In this case the departures between observed moisture uptake and predictions of classical diffusion can be explained in the context of a continuum damage model which was developed recently [10].

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